

Polymer-based fluorescence sensor incorporating triazole moieties for Hg²⁺ detection via click reaction

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ABSTRACT

The polymer could be obtained by the polymerization of 1,4-dibutoxy-2,5-diethynylbenzene (**M-1**) with 1,4-diazidobenzene (**M-2**) via click reaction. The polymer show blue fluorescence. The responsive optical properties of the polymer on various transition metal ions were investigated by fluorescence spectra. Compared with other cations, such as Co²⁺, Ni²⁺, Ag⁺, Cd²⁺, Cu²⁺ and Zn²⁺, Hg²⁺ can exhibit the most pronounced fluorescence response of the polymer. Hg²⁺ can exhibit the most pronounced fluorescence response of the polymer due to triazole moiety in the polymer main chain as the metal binding ligand. The results indicate this kind of conjugated polymer with triazole moiety synthesized by click reaction can be used as a selective fluorescence sensor for Hg²⁺ detection.

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1. Introduction

Conjugated polymers (CPs) used as fluorescence sensors have been gained increased attention due to their high sensitivity and ease of measurement. The high sensitivity of the conjugated polymers originates from the sensory signal amplification which attributed to energy migration along the polymer backbone upon light excitations. An additional advantage of polymer-based fluorescence sensors is that the structure and sequence of the conjugated polymers can be systematically modified to suit for diverse targets by the introduction of the functional groups based on steric and electronic property at well-defined molecular level [1,2]. The research on the polymer-based fluorescence sensor for heavy and transition metal (HTM) ions detection is emerging as an area of current interest in the recent years [3–5]. Among them, mercury and its derivatives are dangerous and widespread global pollutants, and they have caused serious environmental and health problems [6–9]. Many fluorescence sensors for mercury detection have been reported, but most of them are based on small molecules [3,10], and polymer-based chemosensors are very few [11–19]. Therefore, the development of highly selective and sensitive polymer-based chemosensors for HTM ions detection is still attractive.

Click reaction established by Sharpless and co-workers is an efficient tool for the preparation of wide-ranging organic compounds [20,21]. The Copper-catalyzed azide-alkyne click reaction (also termed CuAAC) has had enormous impact on the field of polymer science due to the high efficiency, mild reaction conditions and technical simplicity of the reaction in the last five years. Polymer chemists have widely employed click chemistry in material science and polymer bioconjugation [22–25]. Although a triazole unit which may be used as a potential transition metal coordinating ligand is formed in CuAAC [26], very few polymer-based conjugated fluorescence sensors incorporating triazole moieties examples have been reported. In this paper, we report the synthesis of the conjugated polymer incorporating triazole moieties used as fluorescence sensor for transition metal ions detection via click reaction. Compared with other cations, such as Co²⁺, Ni²⁺, Ag⁺, Cd²⁺, Cu²⁺ and Zn²⁺, Hg²⁺ can exhibit the most pronounced fluorescence response of the polymer using triazole moiety as the metal binding sites. The results indicate this kind of polymer with triazole moiety based on click reaction can be used as a selective fluorescence sensor for Hg²⁺ detection.

2. Experimental part

2.1. Materials

All solvents and reagents were commercially available and analytical-reagent-grade. *para*-Phenylenediol and *para*-phenylenediamine

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were purchased from Aldrich and directly used without purification. 1,4-Diazidobenzene (M-2) could be synthesized from *para*-phenylenediamine by a 2-step reaction according to reported literature [27].

2.2. Measurements

NMR spectra were obtained using a 300-Bruker spectrometer 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR and reported as parts per million (ppm) from the internal standard TMS. FT-IR spectra were taken on a Nexus 870 FT-IR spectrometer. UV–vis spectra were obtained from a Perkin–Elmer Lambda 25 spectrometer. Fluorescence spectra were obtained from a RF-5301PC spectrometer. Thermogravimetric analyses (TGA) was performed on a Perkin–Elmer Pyris-1 instrument under N_2 atmosphere. MS was determined on a Micromass GCT. C, H and N of elemental analyses were performed on an Elementar Vario MICRO analyzer. Molecular weight was determined by GPC with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards. All solvents and reagents were commercially available A. R. grade.

2.3. Preparation of M-1 (Scheme 1)

1,4-Dibutoxybenzene was synthesized according to a reported method [28]. A solution of 1,4-dibutoxybenzene (6.60 g, 29.7 mmol), KIO_3 (2.55 g, 11.9 mmol) and I_2 (8.35 g, 32.9 mmol) in 50 mL acetic acid, 0.9 mL sulphuric acid and 4 mL water was stirred at 80°C for 24 h. After cooling, solution of $\text{Na}_2\text{S}_2\text{O}_3$ was added until the purple color disappeared, then the reaction mixture was poured into 100 mL water and extracted with petroleum ether (3×50 mL). The organic layer was washed with water, and then dried over anhydrous Na_2SO_4 . The solution was evaporated under reduced pressure to give 1,4-dibutoxy-2,5-diiodobenzene (10.3 g, 73.6%) as a white solid. ^1H NMR (CDCl_3 , 300 MHz): δ 7.20 (s, 2H), 3.96 (t, 4H, $J = 6.6$ Hz), 1.83–1.76 (m, 4H), 1.59–1.52 (m, 4H), 1.00 (t, 6H, $J = 7.5$ Hz).

A mixture of 1,4-dibutoxy-2,5-diiodobenzene (3.00 g, 6.33 mmol), $\text{Pd}(\text{PPh}_3)_4$ (366 mg, 0.32 mmol), CuI (241 mg, 1.27 mmol) and trimethylsilyl acetylene (3.58 mL, 25.3 mmol) was dissolved in 15 mL Et_3N and 40 mL THF. The reaction mixture was stirred at 40°C for 48 h under a N_2 atmosphere. The solution was cooled to room temperature, and then the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (2×50 mL). The organic layer was washed with cool water, and then dried over anhydrous Na_2SO_4 . The solution was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) (50:1, v/v) to give 2,5-bis(trimethylsilylethynyl)-1,4-dibutoxybenzene (2.30 g, 87.8%) as a white solid. ^1H NMR (CDCl_3 , 300 MHz): δ 6.91 (s, 2H), 3.97 (t, 4H, $J = 6.3$ Hz), 1.84–1.75 (m, 4H), 1.62–1.49 (m, 4H), 0.99 (t, 6H, $J = 7.5$ Hz), 0.27 (s, 18H). A mixture of 2,5-bis(trimethylsilylethynyl)-1,4-dibutoxybenzene (0.85 g, 2.05 mmol) in 1 mol L^{-1} KOH methanol solution (50 mL) was stirred at room temperature for 1 h. The completion of the reaction was determined by TLC. The reaction mixture was poured into water (20 mL) and extracted with CHCl_3 (2×30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , and then evaporated in vacuo to dryness to give M-1 (0.50 g, 90.9%) as a pale yellow solid. ^1H NMR (CDCl_3 , 300 MHz): δ 6.97 (s, 2H), 4.00 (t, 4H, $J = 6.6$ Hz), 3.35 (s, 2H), 1.83–1.78 (m, 4H), 1.56–1.51 (m, 4H), 0.99 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 153.9, 117.7, 113.2, 82.3, 79.7, 69.2, 31.1, 19.1, 13.7. FT-IR (KBr, cm^{-1}): 3270, 2962, 2921, 2861, 1498, 1465, 1402, 1384, 1221, 1063, 1025. MS (EI, m/z): 270 (29%), 214 (6%), 158 (100%), 102 (11%), 84 (14%), 49 (23%). Anal. calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2$: C, 79.96; H, 8.20. Found: C, 79.90; H, 8.25.

2.4. Preparation of the conjugated polymer (Scheme 1)

A mixture of M-1 (108.0 mg, 0.40 mmol), M-2 (64.0 mg, 0.40 mmol), 10 mol% sodium ascorbate (7.92 mg, 0.040 mmol) and 5 mol% $\text{Cu}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (4.99 mg, 0.020 mmol) was dissolved in the mixed solvents of 10 mL THF, 10 mL *t*-BuOH, and 10 mL H_2O . The solution was stirred at 30 – 36°C for 2 days under N_2 . The solvents were removed under reduced pressure and the residue was extracted with CHCl_3 (2×50 mL). The organic layer was washed with an aqueous NH_4OH solution, water and then dried over anhydrous Na_2SO_4 . After the solution was removed, the resulting polymer was precipitated into methanol, and then filtered and washed with methanol several times. Further purification could be conducted by dissolving the polymer in CHCl_3 to precipitate in methanol again. The polymer was dried in vacuum to give 138.0 mg as a yellow solid in 80.2% yield. $M_w = 8400$, $M_n = 7080$, $\text{PDI} = 1.2$. ^1H NMR (300 Hz, $\text{DMSO}-d_6$): δ 8.97 (s, 1H), 8.84 (s, 1H), 8.22–7.97 (m, 2H), 7.83–7.22 (m, 4H), 4.35–4.10 (m, 4H), 1.94–1.87 (m, 4H), 1.55–1.46 (m, 4H), 1.02–0.94 (m, 4H). FT-IR (KBr, cm^{-1}): 2956, 2931, 2869, 2093, 1525, 1243, 1029. Anal. calcd for $\text{C}_{24}\text{H}_{26}\text{N}_6\text{O}_2$: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.76; H, 6.21; N, 19.43.

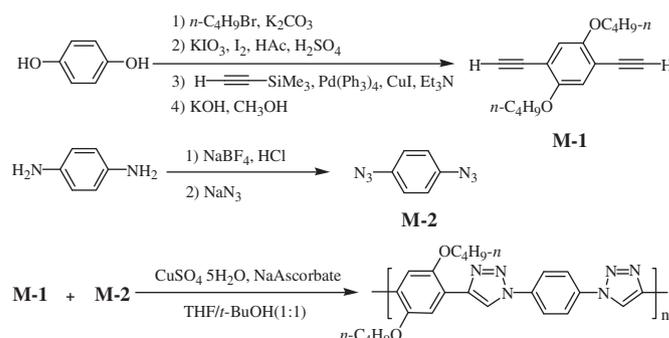
2.5. Metal ion titration

Each metal ion titration experiment was started with a 3.0 mL polymer in CHCl_3 solution with a known concentration ($1.0 \times 10^{-5} \text{ mol L}^{-1}$). Mercury perchlorate salt and other various metal salts (nitrate, $1.0 \times 10^{-3} \text{ mol L}^{-1}$, CH_3CN) were used for the titration. Polymer–metal complexes were produced by adding aliquots of a solution of the selected metal salt to a CHCl_3 solution of the polymer. All kinds of measurements were monitored 2 h after addition of the metal salt to the polymer solutions.

3. Results and discussion

3.1. Synthesis and feature of the conjugated polymer

The synthesis procedures of the monomers 1,4-dibutoxy-2,5-diethynylbenzene (M-1), 1,4-diazidobenzene (M-2) and the conjugated polymer are outlined in Scheme 1. The monomer M-1 could be obtained by a 4-step reaction from the starting material *p*-dihydroxybenzene [28]. M-1 and M-2 could be served as the monomers for the synthesis of the target polymer. In this paper, a typical click reaction condition was applied to the synthesis of the polymer [21,29]. The polymerization could be carried out under mild reaction conditions in THF/*t*-BuOH (1:1, v/v) solution in the presence of a catalytic amount of sodium ascorbate (10%mol) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (5%mol) with a good yield as high as 80.2%. The number-average molecular weight (M_n) and the weight-average



Scheme 1. Synthesis procedures of the polymer sensor.

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